An X-ray Scattering Study of Water-Conditioned Injection-Molded Starch during Isothermal Heating

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ABSTRACT: The *in situ* structure variation of injection-molded starch (as processed and after water conditioning) during heat treatment was investigated by means of wide-angle X-ray scattering using synchrotron radiation. Results confirm that the crystal structure of potato starch is destroyed after injection molding, while as-processed corn starch preserves some degree of crystallinity. This residual crystallinity in corn starch is related to the crystalline Vh-form, made of complexes of amylose with lipids. Furthermore, it is shown that both starch types can develop crystallinity by water conditioning: potato starch yields the crystal B-form, while corn starch yields the crystal A-form coexisting with the persistent Vh-form. Upon isothermal heating of samples under vacuum, a rapid decrease of crystallinity, which is a function of both time and treatment temperature, is detected. Crystallinity variations are discussed in terms of water evaporation, the leveling-off values of crystallinity being dependent on the temperature of the isothermal treatment. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 17–21, 2003

Key words: injection molding; polysaccharides; WAXS

INTRODUCTION

Starch is a thermoplastic biopolymer that has been traditionally used in the food industry. However, starch has also some valuable features that makes of it a good candidate to substitute the synthetic polymers in some of their applications, i.e., low cost of production, ease of processing by conventional methods, and biodegradability.

From the structural point of view, starch is a complex material that presents several levels of organization, and its properties have been widely studied.[1–4] The gelatinization process[3] and the liquid crystalline properties of potato starch[4] have been studied by means of X-ray scattering using synchrotron radiation. From the view point of processing, the influence of several methods, compression or injection molding, etc., on the structure and surface mechanical properties of native potato starch has recently been reported.[5] In addition, the conspicuous effect of the water on the mechanical properties of the injected molded starch and cement clay–starch composites has also been evidenced.[6]

It is well known that starch can show different crystalline structures, depending on its botanical origin. Among them, the A and B structures are the most common ones. The type A-structure, which is typical for starch obtained from cereal plants (wheat, corn, etc.), corresponds to a close packing of starch double helices interconnected by water molecules.[7] The structure of the type B-starch, mainly present in tubers,[8] shows a cylinder-like structure of double helices containing crystal water molecules in the center cavity. There are other crystalline structures, i.e., Vh or E, that appear under special circumstances. The Vh-structure mainly results from the complexing of amylose with compounds as lipids, aliphatic alcohols, or iodine.[9] Lipids are present mainly in cereal starches, and are known to be able to complex with amylose under special conditions, namely moisture content, and temperature.[10] The E-form has been observed in starchy substrates extruded in low moisture conditions.[11]

The objective of the present study is to investigate the structure changes of injection-molded potato and corn starch, as processed and after wet conditioning, *in situ* during isothermal heating (under vacuum) by means of wide-angle X-ray scattering using synchrotron radiation.

EXPERIMENTAL

Materials

The present study includes the analysis of injection-molded starch samples of two different origins: potato starch and corn starch, both kept at room conditions and conditioned in a wet atmosphere (95% of humidity).

Starch samples were injection molded (employing an ARBURG-Allrouder 250S) in two different ways:

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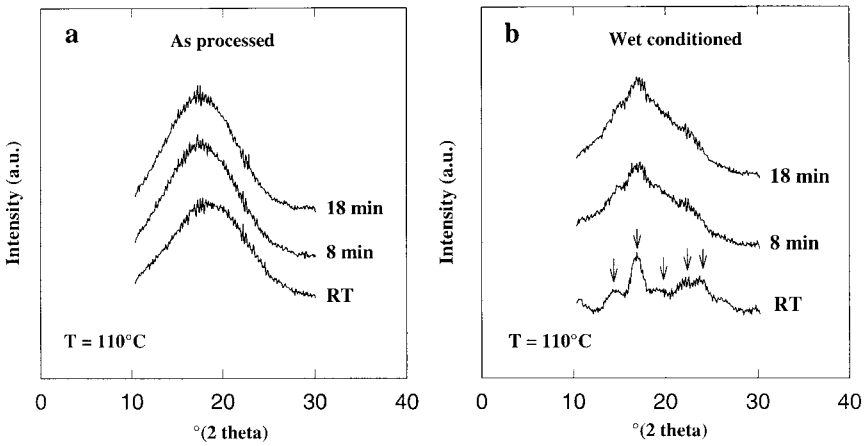

Figure 1 WAXS patterns of injection-molded potato starch samples: (a) as processed, and (b) after wet conditioning, before (room temperature) and during isothermal heating at $T = 110°C$.

(a) using a conventional dumb-bell mold, and (b) by elongational flow injection molding (EFIM). The latter is a processing method that yields high strength materials by inducing an elongational flow during the injection process.[12] Two molding temperatures, T_i, were used: 125 and 140°C. In what follows, unless otherwise stated, we will refer to the samples prepared by elongational flow injection molding at $T_i = 140°C$, using an injection rate of 3 cm/s.

Some of the molded samples were kept in a wet atmosphere (95% of humidity for ≅18 h), just before X-ray experiments were performed. These samples will be called "wet conditioned" in contrast to the "as-processed" ones. The as-processed samples contain about 11–14 wt % of water. After wet conditioning the change in mass, as water is further taken up, is of 20 wt %.[13]

Techniques

WAXS experiments were performed using a double focusing camera for the synchrotron radiation source at the polymer beamline at HASYLAB, Hamburg. The wavelength used was 0.15 nm with a band pass of $\delta\lambda \sim 5.10^{-3}$. The accumulation time per frame was 30 s.

In situ scattering patterns of the starch samples (both as-processed and wet conditioned) were recorded during the isothermal heating in vacuum at various temperatures T (80–180°C) The samples were kept at room temperature for 2 min; thereafter, they were heated up in 30 s to the selected T, and finally maintained at this temperature for times $t > 20$ min. The X-ray patterns recorded for each one of the isothermal experiments were analyzed by means of a curve fit program.

A crystallinity index was estimated as the ratio of the amplitude of the most intense crystalline peak (at about 16.8° (2θ) for the A or B forms, and at 19.6° (2θ) for the Vh form, respectively), to the sum of the amplitude of the amorphous halo plus that of the crystalline peaks.

RESULTS AND DISCUSSION

Structure of potato starch

Influence of heating conditions

Figure 1 shows the evolution upon heating ($T = 110°C$) of some selected WAXS patterns of potato starch for, both, the "as-processed" samples [Fig. 1(a)] and the "wet conditioned" ones [Fig. 1(b)]. The starting WAXS patterns, taken at room temperature, are also shown. Figure 1(a) reveals that the as-processed sample is amorphous. This result is in accordance with previous X-ray measurements,[5] indicating that the crystalline structure of native potato starch is completely destroyed after injection molding. In addition, the as-processed material remains amorphous during the heating process. However, if the moldings are kept in a wet atmosphere (wet conditioned starch) [Fig. 1(b)], potato starch is capable to develop a crystalline structure due to a molecular reorganization favored by the penetration of water.[14] In the present experiments the total water content reached values above 30 wt %. The positions of the main reflections, indicated by the arrows, at 14.5, 16.9, 19.8, 22.1, and 23.9° (2θ), correspond to the B-form. Figure 1(b) also shows that the crystallinity of the initial structure at room temperature (RT) rapidly decreases upon the isothermal treatment.

Figure 2 illustrates the crystallinity index variation as a function of time for the "wet conditioned" injection-molded potato starch samples heated at different temperatures. As stated in the Experimental part, during the first 2 min (see time axis in Fig. 2), the sample is hold at room temperature. The fluctuation of the initial crystallinity values (Fig. 2) could be related to the inhomogeneities of the injection-molded samples,

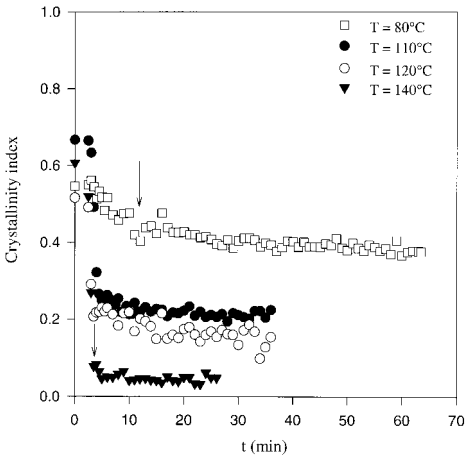

Figure 2 Crystallinity index of wet conditioned injection-molded potato starch as a function of heating time for different temperatures.

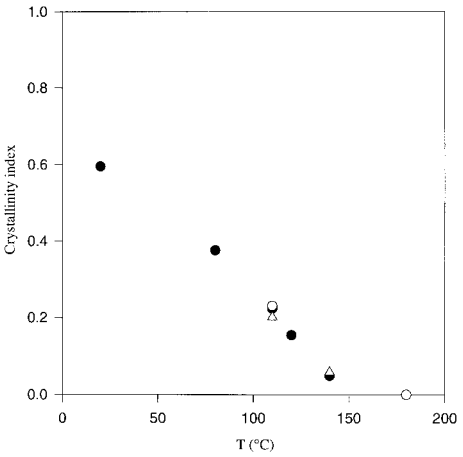

Figure 3 Plot of the leveling-off crystallinity values as a function of the treatment temperature of wet conditioned starch samples. ○, ●: injection-molded potato starch (T_i = 125 and 140°C, respectively). △: injection-molded corn starch, T_i = 140°C.

which affect the interaction of sorbed water after wet conditioning. It can be seen that, while for T = 80°C only a slight crystallinity decrease is observed, for temperatures $T > 100$°C there is a sharp initial decrease of crystallinity during the first 3 min of thermal treatment. The initial decrease of crystallinity is larger the higher T-value used. The rapid initial decrease of crystallinity in Figure 2 could be related to the removal of unbound and some structural water that maintains the three-dimensional order in starch. For T = 80°C, most of the structural water is still retained, thus giving, as a result, a high level of final crystallinity. On the contrary, for higher T values the structural water is more efficiently removed, and consequently, the final crystallinity level is continuously reduced with the increasing T. In consonance with these results, the limiting values for the relative weight-loss measured at different temperatures, are shown to be larger the higher the T-value used.[15] The leveling-off crystallinity values observed show a gradual decrease with T as depicted in Figure 3 (filled circles). These values should be related to the structural water remaining in the sample. Calorimetry experiments on similar samples support the presence of water for starch heated at $T > 100$°C. The thermograms describe the behavior of water molecules in terms of the evaporation from the sample.[13] Thus, the broad endothermic peak observed at ~100°C, shows an asymmetry towards the high T side up to near 200°C,[13] indicating the gradual removal of water in the temperature range investigated.

For the wet conditioned samples processed at a different temperature (T_i = 125°C), a similar crystallinity decrease was observed. Some data for the latter samples isothermally heated at 110 and 180°C are also shown in Figure 3 (open circles). According to Figure 3, the crystallinity developed in wet conditioned potato starch seems to persist up to near 150°C.

Influence of mold processing conditions

Figure 4 shows the crystallinity variation observed at 140°C on wet conditioned potato starch samples processed using a conventional and an EFIM mold. A similar behavior is observed for both samples. However, the final crystallinity values are smaller in the case of a normal mold than in the case of an EFIM one. One may think that the EFIM moldings, having a higher strength, could develop better-ordered crystalline domains with a higher thermal stability than those of the normal moldings.

As it was mentioned above, the injection temperature T_i apparently has no effect on the crystallinity evolution of the samples upon isothermal treatment (see Fig. 3).

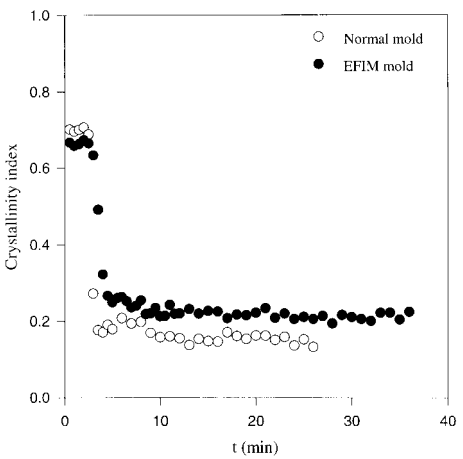

Figure 4 Variation of the crystallinity index for wet conditioned potato starch as a function of heating time at T = 110°C: Influence of mold geometry.

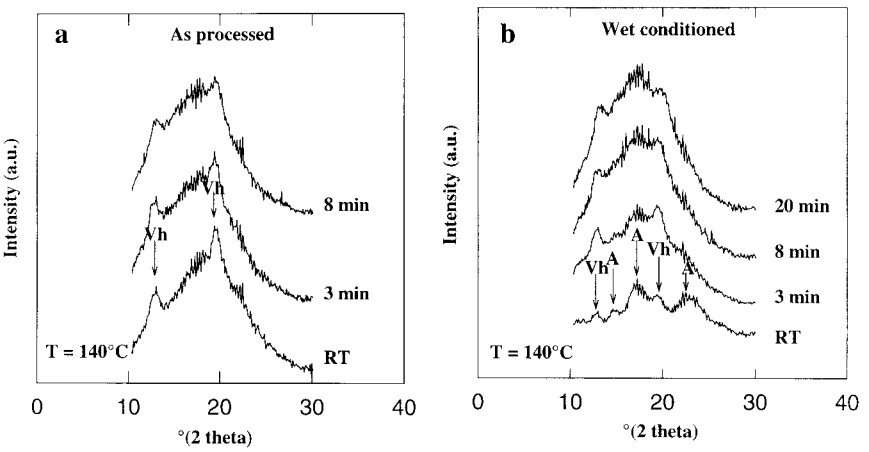

Figure 5 WAXS patterns of injection-molded corn starch samples: (a) as processed, and (b) after wet conditioning, before and during isothermal heating at $T = 140°C$.

Structure of corn starch

In contrast to potato starch, the as-processed corn starch samples show some indication of crystallinity [Fig. 5(a)]. Two well-resolved peaks [at 12.9 and 19.6° (2θ)] reveal the presence of the crystal Vh-form. As it is known, the Vh-form is associated to the presence of a complex of crystalline amylose single helices containing lipids. The occurrence of these stable complexes in corn starch may explain the appearance of the crystal Vh-form after processing, in contrast to potato starch, free of lipids. From the literature,[16] it seems that the injection molding conditions induce the crystallization of the Vh-form in corn starch samples.

In these samples, the crystallinity slightly decreases from about 0.25 down to 0.2 during heating of the processed materials. The final crystallinity index (approx. 0.2) seems to be independent on the heating temperature.

On the other hand, the processed material develops crystallinity upon wet conditioning, as potato starch does [Fig. 5(b)]. The new reflections, at about 14.9, 17.3, and 23° (2θ) here are related to the crystal A-form. The crystallinity indexes corresponding to the A-form and Vh-form, measured from the room temperature X-ray pattern, are 0.45 and 0.25, respectively. This means that the amount of the Vh-form, already present in the as processed samples, seems not to be modified by the wet conditioning of the processed corn starch.

Concerning the thermal stability of both crystalline forms of corn starch, the X-ray diffractograms presented in the Figure 5(b) also reveal a quick development of the amorphous halo because of the preferential disappearance of A-form. Figure 6 shows the time variation of the crystallinity index corresponding to the A-form for two isothermal treatments. Comparison of the results shown in Figure 6 for corn starch with those corresponding to potato starch (Fig. 2) reveal a similar thermal stability for both A- and B-forms. In fact, the final crystallinity values observed for the A-form of corn starch are also shown in Figure 3 (open triangles). It can be seen that these values clearly match with those presented for potato starch (open and filled circles).

On the other hand, after isothermal treatment of wet conditioned corn starch, the amount of the Vh-form is only slightly reduced. Thus, its crystallinity index (not shown here) decreases from about 0.25 down to 0.18. This final value, however, is similar for the two temperatures investigated.

CONCLUSIONS

1. Although X-ray diffractograms of the "as-processed" injection molded potato starch are amorphous, those of corn starch exhibit characteristic reflections of the crystal Vh-form, which is stable

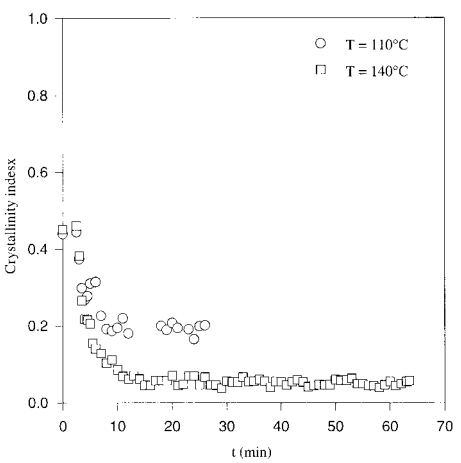

Figure 6 Crystallinity index of the A-form in wet conditioned injection-molded corn starch as a function of heating time for two temperatures.

under both the thermal and wet conditioning treatments employed.

2. Upon wet conditioning of the injection molded samples (involving a water uptake of ~20 wt %), there is a crystallinity development by chain rearrangement favored by the water sorption. As a result, the characteristic crystal forms A and B are well resolved in both corn and potato starch, respectively.
3. During isothermal treatment under vacuum, the crystal forms A and B of injection-molded corn and potato starch are destroyed. The final crystallinity values are lower the higher are the temperatures used, and tend to zero for temperatures $T \geq 150°C$.
4. The crystallinity development upon "wet conditioning" of injection-molded starch as well as the loss of crystallinity during heating of samples can be related to the exchange of that water, which is responsible for building up either the A and B crystal forms.

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